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## Diamond ATR and Calibration Transfer for Biodiesel-Blend Analysis by ASTM D7371-14



### Introduction

#### Biodiesel and Biodiesel-Blend Analysis

The need for sustainable fuel sources has led to an increasing global emphasis on fuels produced from renewable, biological

sources. Biodiesel is one such fuel, and consists of fatty acid methyl esters (FAMES) produced from vegetable oils or animal fats via a transesterification reaction. Biodiesel is seldom used neat (B100), typically being blended with fossil diesel at ratios from 5% v/v (B5) to 30% v/v (B30). Verifying the FAME content of diesel-fuel blends is an important aspect of quality control and auditing of blending and distribution operations. Because FAME has a strong infrared absorption at  $1745\text{ cm}^{-1}$  due to the ester

carbonyl group, infrared spectroscopy is an excellent technique for this analysis, and there are EN and ASTM® standard test methods describing the procedure.<sup>1,2</sup>

The PerkinElmer Biodiesel IR FAME Analyzer<sup>3</sup> consists of a Spectrum 3™ FTIR spectrometer with an attenuated total reflection (ATR) accessory featuring either a diamond or zinc selenide (ZnSe) crystal. In addition to the Spectrum 10 software, which includes a dedicated biodiesel-analysis module and detailed standard operating procedures (SOPs), the system is provided with a “starter calibration”, covering the full range from 0% to 100% FAME. This application note describes how the supplied calibration can be optimized to give peak performance in a particular installation, without resorting to a full recalibration.

## Diamond ATR

The recently published ASTM® standard D7371-14 involves the use of an ATR sampling accessory with a zinc selenide (ZnSe) crystal. ZnSe has a suitable refractive index and its absorption edge is at a sufficiently long wavelength, but it is relatively easy to damage, and care is required while cleaning. Diamond is an increasingly popular material for ATR because it has a similar refractive index yet is far more robust. In this application note, we demonstrate the suitability of the PerkinElmer Universal ATR (UATR) accessory with a 9-bounce diamond top-plate for this analysis.

## Calibration Transfer

ASTM® D7371-14 uses a set of three partial least squares (PLS) regression models (one for each of the concentration ranges 0–10, 10–30 and 30–100% v/v) and large calibration and validation sets (~40–60 standards). Even with the convenience of ATR sampling, calibration is a very time-consuming operation. The ability to develop a calibration on one instrument and transfer it to others can greatly speed up deployment of multiple analyzers, or allow the use of a vendor-supplied calibration.

There are several sources of instrument-to-instrument and sampling accessory-to-accessory variation that can impede a direct calibration transfer between FTIR systems. The wavelength scale and instrument lineshape can vary due to factors such as vignetting by the accessory. With the Biodiesel IR FAME Analyzer, these variations are treated by the Absolute Virtual Instrument (AVI) algorithm<sup>4</sup> that standardizes a measured spectrum of methane against data from the HIT RAN database.

In addition, there are several factors that can cause a difference in sensitivity—that is, variation in absorbance values for the same sample. The effective path-length for an ATR measurement depends on the incidence angle of the light at the interface between the crystal and the sample. In every instrument, there is a distribution of incidence angles around the nominal value, and this distribution can vary slightly between instruments and accessories. Because ATR path lengths are on the order of micrometers, small scratches and imperfections in the crystal surface can have unpredictable effects on sensitivity. This is not a problem with diamond, since it is very difficult to scratch, but is certainly an issue with zinc selenide crystals.

## Methods

### Calibration Transfer

There is extensive literature on methods for calibration transfer, and some very sophisticated algorithms are available. In this work, however, we have employed two of the more simple methods. Both of these methods involve measuring a small number of calibration transfer standards (FAME blends of known composition) on the new instrument.

The Biodiesel IR FAME Analyzer is provided with calibrated PLS models developed according to the ASTM® D7371-14 specification. SOP's are provided giving details of how to conduct calibration transfer using two different approaches.

In the first method, bias correction, the FAME values are predicted from the spectra by the provided models, and a straight line is fit through the true and predicted FAME values. Both the slope and intercept of this line are used to correct future predictions. This functionality is built into the PerkinElmer Quant+™ software used for the calibration.

In the second method, model updating, the spectra of the calibration transfer standards measured on the new instrument are incorporated into the chemometric model directly as calibration standards, and then the model is recalibrated.

In this application note, we describe work undertaken to assess the suitability of these two calibration-transfer approaches for the ASTM® D7371-14 application.

## Experimental

The ASTM® D7371-14 calibrations were initially conducted on a single PerkinElmer Spectrum™ 100 system\* with both 9-bounce diamond UATR and ZnSe horizontal ATR (HATR) accessories. The UATR calibration was transferred to five separate Spectrum 100 systems, and the HATR calibration to two. The same pool of validation standards was used for each instrument, and comprised 21 standards for each of the three concentration ranges. Of these, 7 were used (per model) for the calibration transfer and the remainder to assess the performance of the transferred model.

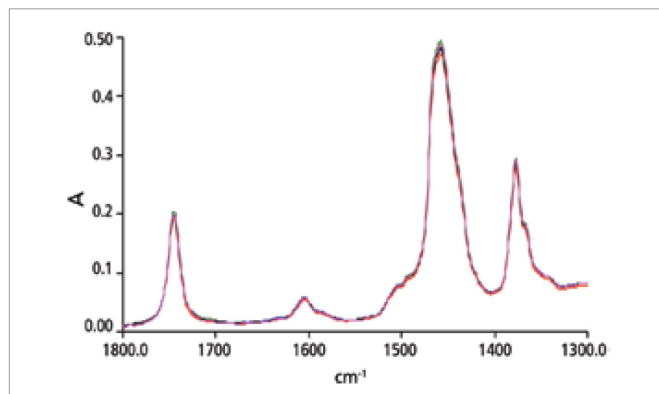


Figure 1. Spectra of a 9.4% v/v FAME sample measured on five Spectrum 100 instruments with 9-bounce diamond UATR accessories. The relative range of measured values for the carbonyl peak height is 2%.

\* The Spectrum 3 FTIR now supercedes the Spectrum 100 and Frontier, and has identical optical performance characteristics.

## Results and Discussion

Spectra of a 9.4% v/v FAME sample measured on the five UATR instruments are shown in Figure 1. The spectra overlaid each other almost exactly, but there is a ~2% variation in the height of the carbonyl peak. This variation corresponds to a small but significant error if the calibration were used without modification.

Figure 2 shows the validation results of the original, bias corrected, and updated models for a single UATR instrument. The linear structure evident in the residuals for the uncorrected plot is effectively removed by either calibration-transfer technique, with a concomitant improvement in the standard error of qualification (SEQ). The SEQ is a measure of the average error encountered in the validation. Here, this quantity is calculated considering only samples with concentration <20% v/v FAME: this is to enable easy comparison with the ASTM® D7371-14 specifications, which state that an instrument is qualified to perform the analysis only if its SEQ is not significantly greater than the value derived from their round robin studies, given as 0.21% v/v multiplied by a factor determined by an F-test. Given the number of samples in the present validation set, the limit becomes 0.27% v/v. In the example shown here, the uncorrected calibration would fail this test, while the two corrected calibrations would pass.

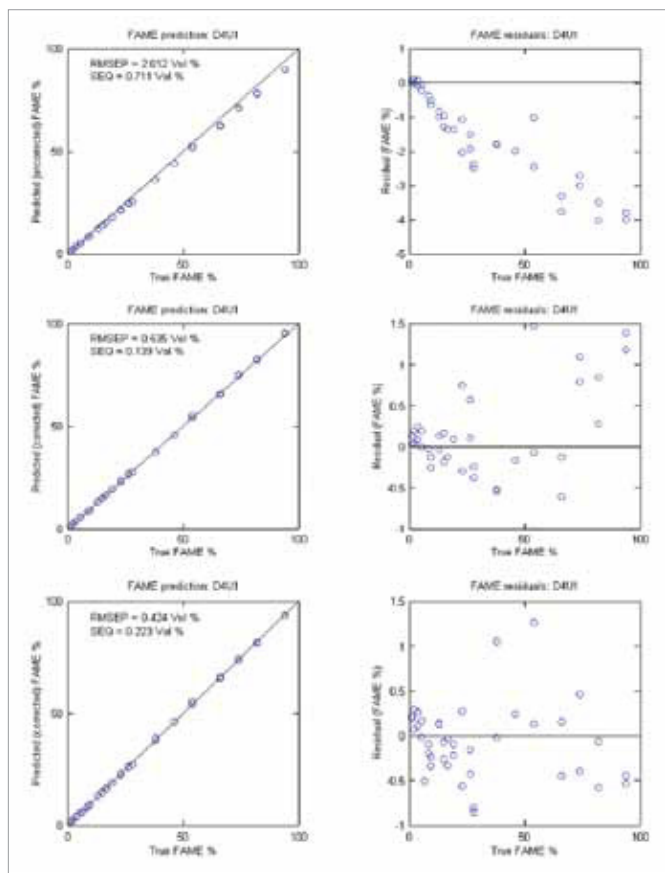


Figure 2. Calibration transfer results (predicted-vs-true and residual plots) for one UATR instrument. Top: uncorrected predictions; Center: bias correction; Bottom: model updating.

A summary of the results obtained for the other instruments is presented in Table 1. All of the UATR instruments were validated to perform the analysis in terms of the ASTM® D7371-14 requirements, regardless of which calibration transfer approach was used. Bias correction tended to give slightly better results for the UATR systems and dramatically better results for the HATR systems. This is likely due to the greater potential for sensitivity differences between HATR systems: a simple sensitivity difference is directly modelled by the bias correction, but cannot be completely corrected simply by adding a few standards to the model.

Table 1. Summary of calibration transfer results. SEQ100 is the SEQ calculated using the full validation set; SEQ20 was calculated using only samples with <20% v/v FAME (both are in units of % v/v FAME). A system is considered validated according to ASTM® D7371-14 if SEQ20 <0.27% v/v.

System	Bias Correction			Model Updating		
	SEQ <sub>100</sub>	SEQ <sub>20</sub>	Validated?	SEQ <sub>100</sub>	SEQ <sub>20</sub>	Validated?
A (UATR)	0.47	0.22	Yes	0.62	0.23	Yes
B (UATR)	0.26	0.18	Yes	0.36	0.18	Yes
C (HATR)	0.38	0.14	Yes	0.73	0.54	No
D (UATR)	0.34	0.24	Yes	0.57	0.25	Yes
E (HATR)	1.24	0.21	Yes	0.99	0.62	No
F (UATR)	0.40	0.24	Yes	0.39	0.22	Yes
G (UATR)	0.54	0.14	Yes	0.42	0.22	Yes

## Conclusions

When using the AVI algorithm for spectral standardization, a simple bias-correction calibration transfer is sufficient to provide excellent performance of the supplier “starter” calibration on a new instrument.

The biodiesel validation samples used the same FAME source as the calibration standards, so this work addresses only the differences between instruments and accessories. FAME from a different source will have a different distribution of fatty acid chains and potentially a somewhat different infrared spectrum, and the suitability of a simple calibration transfer requires further investigation.

It must be noted that the ASTM® D7371-14 document<sup>1</sup> makes no mention of calibration transfer, and thus implies that for strict adherence to the standard, it is necessary to calibrate each instrument individually. For situations where the requirement is simply to demonstrate good performance on validation standards, however, calibration transfer can provide a valuable time saving.

## Acknowledgements

The calibration models for the ASTM® D7371-14 method were developed for PerkinElmer by Dave Wooton of Wooton Consulting, Beaverdam, VA. Dr. Wooton also supplied the validation standards.

## References

1. ASTM® International D7371-14: Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method).
2. European Standard EN 14078:2014: Liquid petroleum products – Determination of fatty acid methyl esters (FAME) in middle distillates – Infrared spectroscopy method.
3. "Biodiesel Blend Analysis by FTIR (ASTM® D7371-14 and EN 14078)" Ben Perston and Nick Harris, PerkinElmer, 2009.
4. "Absolute Virtual Instrument (AVI)" PerkinElmer, 2005.